Characterization of Nanocrystalline Metal Selenide Powder and Thin Films

Ph.D
Proposal

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INTRODUCTION

Nanotechnology is the relatively new area of science that has generated excitement worldwide. Working at nanoscale, scientists are creating new tools, products and technologies to address some of the world's biggest challenges. Nanoscience is a combination of nano, meaning "dwarf" and the word science. Nanometer refers to 10^{-9} or one billionth of a meter. Nanoparticles are larger than individual atom and molecules, but are smaller than bulk solid, hence they obey neither absolute quantum chemistry nor laws of classical physics and have properties that are different from those expected. Properties not seen on a macroscopic scale are now becoming important on nanoscale such as: optics, magnetism, surface reactivity and thermodynamics.

In nanoparticles, the properties (physical, chemical, biological etc.) can be selectively controlled by engineering the size, morphology, and composition of the particles. Nanomaterials are known to exhibit markedly different properties compared to micron sized ones. These new substances will have enhanced or entirely different properties from their bulk counterparts. The main factor cause the properties of nanomaterials to differ significantly from other materials are increased relative surface area, it can change or enhance properties such as reactivity, strength and electrical characteristics. As growth and catalytic chemical reactions occur at surfaces, this means that a given mass of material in nanoparticulate form will be much more reactive than the same mass of material made up of larger particles. It has been shown that the various material properties such as electrical, mechanical, optical, magnetic etc. are highly influenced by the fine-grained structure and there is generally improvement in the concerned properties. Using a variety of synthesis methods, it is possible to produce nanostructured materials in the various forms like: thin films, powder, quantum wires, quantum wells, quantum dots, etc.

In general, nanocrystalline materials can be synthesized either by consolidating small clusters or breaking down the bulk material into smaller and smaller dimensions. Thus, nanosynthesis methods fall into two classes, namely called *bottom-up* and *top-down*. Bottom-up approach is to collect, consolidate and fashion individual atoms and molecules into the structure. The top-down method starts with the large scale object or pattern and gradually reduces its dimension or dimensions.

Preparation of nanomaterial samples that are uniform in composition, size, shape, internal structure and surface chemistry is essential to successfully map their

size-dependent material properties. Only with careful characterization, the size-dependent magnetic, optical and electronic properties of the nanocrystals in the sample can be discovered. These nanocrystal samples may then be used as the building blocks for close-packed nanocrystalline solids. The synthesis of nanophase or cluster assembled materials is usually based upon the creation of separated small clusters which are then fused into a bulk material or as a thin film or even by embedding into a solid matrix like polymers or glass either in a disordered manner or in an ordered array. There is a need to learn how to manipulate nanosized particles and form the ensemble into periodically ordered particulate materials for application into devices of the special physical properties.

The nanomaterials in principle may be metallic, semiconductors, glass, ceramic or polymer. Amongst the various types of nanomaterials semiconductor nanoparticles have been widely investigated. This is quite understandable as metals and ceramics or insulators have very limited applications. They either have very high (metals) or very low (ceramics) conductivities. The photosensitivity is limited in case of these materials. They exhibit strong size dependent properties that may provide insight into the scaling limits of magnetic storage and microelectronics, key component in information technology. In nanometer scale structures, finite size effects give rise to novel electronic, magnetic, optical, and structural properties.

The synthesis of binary metal chalcogenides semiconductors in a nanocrystalline form has been a rapidly growing area of research due to their luminescent properties, quantum size effect and other important physical and chemical properties. Particularly the metal selenides, CdSe and SnSe have received considerably more attention. These are typical direct band gap semiconductors, which has been a model material in the studies of quantum size effects. By appropriate choice of MSe nanocrystal size the absorption edge can thus be made to fall anywhere in visible region. The semiconductor MSe compounds has attracted a lot of attension due to its great technological interest as optical and optoelectronic materials. SnSe is widely used as holographic recording systems, infrared electronic and memory switching devices, photoelectrical cells and decreasing the photocorrosion process. Nanocrystalline semiconductors offer a wide variety of possible applications in nanoelectronics and nanophotonics, optical and optoelectronic devices, LED’s or as resonators in wave guide. It has found applications in solar cells, gamma-ray detectors, TFTs, PEC cells.

REVIEW OF LITERATURE

Pejova et al. [1] developed a chemical route to orthorhombic nanocrystalline photoconducting tin (II) selenide quantum dots in thin film form and studied the structural and optical properties of the synthesized materials. An increase in average crystal size was found on thermal treatment accompanied by slight enlargement of the unit cell parameters. They characterize the as-deposited films as indirect band gap with an additional electronic transition of a direct type. **Bernardes-Silva et al. [2]** studied the thermal treatment, in nitrogen flow for crystalline tin selenide semiconductor synthesized by a chemical route. They obtained a mixture of tin oxides and orthorhombic tin selenide. **Zainal et al. [3]** deposited polycrystalline tin selenide thin films on indium tin oxide glass slides. Different studies show a p-type conduction mechanism with optical direct band gap of about 1.25 eV**. Hankare et al. [4-5]** obtained cadmium selenide thin films, on glass substrates, using dip method. Room temperature deposited films were having cubic structure with an energy gap equal to 1.82 eV. They also deposited reddish brown, uniform, well adherent, well defined grained and nearly stoichiometric lead selenide thin films on glass substrate by a modified chemical bath deposition method (CBD). The films were polycrystalline in nature with FCC structure. Room temperature electrical conductivity of the film was of the order of 10^{-3} $(\Omega\,\mathrm{cm})^{-1}$ with p-type conduction mechanism. **Nair et al. [6]** presented the chemical bath deposition technique for different semiconducting thin films. They suggested that the effect of annealing the films in air on their structure and composition and on the electrical properties is notable. They also reported that CdS and ZnS films became conductive through a partial conversion to oxide phase, CdSe became photosensitive, SnS was converted to SnO_2, etc. **Levichev et al. [7]** worked on post-growth annealing effect on $CdSe/SiO_2$ thin films grown by rf-magnetron co-sputtering technique. They reported that the nanocrystals size changed from 1.5 to 5 nm by varying the annealing temperature from 550 to 400 °C. Evaporation of Se at high temperatures was invoked to explain this phenomenon. Fowler–Nordheim tunneling mechanism was found to be responsible for carrier transport for samples with bigger CdSe NCs sizes, and which showed better photovoltaic properties. **Farva et al. [8]** synthesized CdSe nanocrystals of 3-4 nm size by hot-injection method. The influence of thermal annealing in air and N_2 atmosphere on the morphology and optoelectronic properties was elucidated. The CdSe nanoparticles showed phase transformation upon annealing in air at 350 ^{0}C

from nanocrystalline sphalerite cubic (ZincBlende) structure to hexagonal (Wurtzite) structure. After annealing in air or N2-atmosphere at 250 and 350°C, respectively, indicated the improvement of crystallinity and surface passivation characteristics of the CdSe nanocrystals. **Shin et al. [9]** studied the effects of different annealing conditions such as atmospheres, temperatures and times on the structural, morphological and optical properties of ZnS thin films prepared on glass substrates. They reported an amorphous structure or poor crystallinity below the optimized annealing conditions of 500°C and 60 min with the exception of the films annealed in N2+H_2S annealing atmosphere. **Choi et al. [10]** synthesized colloidal CdSe nanocrystals through solution process. CdSe nanocrystals showed quantum confinement effects well in solution form. **Kale et al. [11]** grown cadmium selenide nano-crystallites on amorphous glass substrate using chemical bath deposition method at room temperature. The samples were annealed in air. The as-deposited CdSe layers grew in the nanocrystalline cubic phase, with optical band gap of 2.3 eV and electrical resistivity of the order of 10^6 Ωcm. After annealing metastable nanocrystalline cubic phase transformed into stable polycrystalline hexagonal phase. Depending upon temperature, decrease in the band gap and electrical resistivity was observed. **Padiyan et al. [12]** prepared polycrystalline thin films of tin selenide by vacuum deposition at a substrate temperature of 150°C. Annealing the films at 300°C for 2 hours improved the crystallinity. The optical transmission measurement reveals that the SnSe thin films have a direct allowed band gap of 1.26 eV. Electrical conductivity study showed that the conductivity increases with increasing temperature. The photoconductivity measurement indicated the presence of continuously distributed deep localized gap states in this material. **Julien et al. [13]** reported a study of the optical and electrical properties of tin monoselenide SnSe and tin dichalcogenides SnX_2 with X = S and Se. The semiconducting character of the single crystals was investigated by means of resistivity and Hall Effect in the temperature range from 90 to 300 K. The experimental data was fitted using a four-parameter dispersion model based on the factorized form of the dielectric function. **Rao et al. [14]** carried out conductivity, photoconductivity and Hall measurements on vacuum evaporated, air exposed SnSe films of different thicknesses in the temperature range 300K-85K. Photoconductivity has been explained by the trapping of majority carriers at the crystallite boundaries. **Law et al. [15]** describe the structural, optical, and electrical properties of films capped PbSe nanocrystals solids.

Post deposition heat treatments triggered nanocrystal sintering at 200°C, before a substantial fraction of the capping group evaporated or pyrolyzed. The sintered nanocrystal films have a large hole density and are highly conductive. The chemically treated films were oxidized rapidly in air to yield highly conductive p-type nanocrystal solids. **Shyju et al. [16]** deposited CdSe thin films on the glass substrates by chemical bath deposition method. The structural, optical, morphological and electrical properties of as deposited and annealed samples were studied. The phase change of CdSe from cubic to hexagonal after annealing at 350° C was confirmed. They reported a increase in particle size after annealing at a higher temperature. The homogeneous crystalline grains were observed. The as-deposited and annealed CdSe films exhibit negative Hall coefficient, which confirmed n-type conductivity. **Esparza-Ponce et al. [17]** used an ammonia-free chemical-bath deposition to obtain CdSe thin films on glass substrate. The films thickness was in the range of 400–500 nm with a growing time of 4 h. The films obtained at bath temperatures of 70 and 80 ◦C had the hexagonal structure (wurtzite type), with crystallite size of about 20 nm. Room temperature deposition results in films with the cubic structure and crystallite size of about 4 nm. **Mehta et al. [18]** presented the chemical bath deposition of spherical zinc selenide nanocrystalline thin films on non-conducting glass substrates. X-ray diffraction studies revealed that the deposited ZnSe is nanocrystalline with a mixture of hexagonal and cubic phase. They demonstrated the effect of the deposition temperature and reactant concentration on the structural, optical and electrical properties of ZnSe films. **Kang et al. [19]** reported the effect of the pH on structural, morphological, and optical properties of polycrystalline zinc sulfide (ZnS) thin films with a wurtzite (hexagonal) structure. The sample deposited with pH 5 and 5.5 was compact and uniform. The transmission spectrum of ZnS thin films having thickness from 30 to 220 nm indicated a good transmission characteristic with an average transmittance of 70–85%.

By reviewing the work of these researchers, we have observed that main emphasis is on the structural and optical properties of different semiconducting nanomaterials. Less work is being reported on detailed electrical properties of nanomaterials. The comparison between the properties of nano crystals in powder form and thin films is missing.

OBJECTIVES

1. To prepare MSe (M = Sn/Cd/Pb/Zn) nanocrystals in powder and thin film form.
2. The MSe nanomaterials will be characterized by using following:
   (a) Structure studies
   (b) Optical Properties.
   (c) Electrical Properties.
3. To study the effect of different deposition parameters on MSe nanocrystals.
4. To study the effect of post deposition annealing on MSe nanocrystals.

METHODOLOGY AND PLAN OF WORK

1 (a) Preparation of MSe Powder

The semiconducting MSe powder will be prepared using chemical bath technique. Firstly, the Se in source will be prepared using selenide ion source and selenium powder (99.9% pure) with anhydrous sodium sulphite (Na_2SO_3) in distilled water. It will be sealed and kept overnight and then filtered to obtain a clear solution. After this an aqueous solution of MSe will be prepared by dissolving metal(s) acetate, capping agent and sodiumselenosulphate in distilled water and stirring the resulting mixture at a constant temperature. The solid phase will be isolated by filtration and finally dried in hot bath, from the residue solution. This solid phase (powder) consist of MSe nanocrystals.

1 (b) Preparation of MSe Thin Films

The semiconducting MSe nanocrystalline thin films will be deposited on glass substrates using chemical bath deposition method. The substrates will be boiled in chromic acid, washed with detergent rinsed in acetone and finally cleaned with double distilled water before use. The substrates will be heated to 120 ^{o}C to remove any moisture or methanol present. The substrate will be maintained in contact with dilute chemical bath containing metal and Se ions.

2 (a) Structure Studies

Structure properties will be studied by using X-ray diffraction, SEM/TEM or Fourier Transform Infra Red (FTIR) Spectroscopy. XRD is a good technique to determine the particle size and strain distribution in thin films. To access the size, microstructure and morphologies of the particles, transmission electron microscopy

imaging is an efficient way to obtain images of the surface of a specimen. Surface information is obtained by scanning probe in which the trajectory of electron beam is directed across the region of particular interest on the surface. FTIR is one of the most powerful tools available to the chemist for identifying organic and inorganic compounds.

2 (b) Optical Studies

Tauc method is very important method to study the optical properties of nanocrystals. Here absorption coefficient, $\alpha = -lnT/d$ with T is the percentage transmission of light, is calculated from transmission curves. From these optical parameters, the optical gap, E^{g}_{opt}, can be determined.

2 (c) Electrical Studies

By studying electric properties one can check the ohmic and non-ohmic behavior. The electrical conductivity, of the film deposited under the optimum deposition conditions, measured at different temperatures yield good information about conduction mechanism and activation energy of materials.

Photoconductivity measurement technique is a valuable diagnostic tool for the material quality. It may be used to determine the energy distribution of various species of gap states. In steady state photoconductivity, light is illuminated on the sample until the steady state is reached. In transient photoconductivity measurements, light is illuminated to the thin film and the rise and decay of photocurrent is measured.

3 Effect of different deposition parameters on the MSe nanocrystals

It has been observed that the deposition parameters have a profound effect on the particle size and on the different properties of nanocrystalline thin films. The effect of deposition parameters (substrate temperature/pH/deposition time) will be studied on the different properties of MSe nanomaterials.

4 Effect of post deposition annealing on the MSe nanocrystals

The effect of thermal annealing on the electrical and optical properties of nanostructured thin films of MSe will be studied. These studies will be performed on as-deposited and thermally treated nanocrystalline MSe thin films in order to elucidate the nature of the changes in composition in these films.

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